DRAFT RSET ISSUE PAPER #6 – PCB Analysis

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(tthornburg@anchorenv.com); August 10, 2004

QUESTION/ISSUE: PCB Analysis.

DISCUSSION:

Background: Currently the DMEF contains screening levels (Screening Levels (SLs), Maximum Levels (MLs), and Bioaccumulation Triggers (BTs)) for PCBs in sediments based on total PCBs. Recent advances in risk assessment for PCBs have indicated that risk to humans and wildlife associated with PCBs may not be well-represented by a total PCB value. In particular, it may only be possible to accurately assess dioxin-like cancer risk using PCB congener data. This may require analyzing for all or a subset of the 209 congeners that are considered polychlorinated biphenyls. On the other hand, risks to benthic invertebrates may be well-characterized by a total PCB value, since it is expected to occur through a narcosis mechanism rather than through the Ah receptor, which is absent in invertebrates.

Issue: The science associated with evaluating bioaccumulative risks from PCBs has advanced considerably since the development of the marine AETs and the original PSDDA BTs, both of which are currently included in the DMEF manual. At this time, there is a consensus among the Analyte Subcommittee that it is time to begin incorporating this new knowledge base into our regulatory framework. Specifically, the committee has discussed whether sediments and/or tissue should be analyzed for PCB congeners, considering the value of the information this would provide us, the practical implications of doing so, and the cost associated with congener analyses.

The cost to analyze for PCB congeners is significantly greater than the cost for standard PCB arochlor or homologue analysis (Table 1). However, this information, particularly in tissues, is considered necessary in order to conduct risk assessments for the bioaccumulative pathways. On the other hand, the committee does not consider it necessary to obtain congener data for sediments, since risks to the benthic community are better modeled through a total PCB (or narcosis-based) pathway. These recommendations affect the SQG and Bioaccumulation Subcommittees' work, who would then need to formulate sediment and/or tissue standards accordingly.

There will be issues related to calculation of site-specific cleanup or dredging criteria based on analysis of tissues and calculation of bioaccumulative risks associated with tissues, if sediments and tissues are analyzed in different ways. However, these issues are unavoidable to some extent even if congeners are analyzed in both sediments and tissues, since the pattern of congeners present in each is affected by disproportionate accumulation of congeners with varying molecular weights. As an alternative, the committee recommends using methods recently developed (Nedoff et al., 2004; NOAA 1989) to estimate total PCBs in tissues from congener data, and back-calculate to sediment concentrations based on these estimates (Table 2). Alternatively, GIS-based methods can be used to evaluate the areas and extent to which PCBs in sediments need to be lowered to reduce overall exposure concentrations within a species' home range to levels that should reduce tissue

concentrations to acceptable risk levels.

Because of the higher costs associated with congener analysis and the more time- consuming procedures associated with collecting tissue data, the determination of the need to evaluate this contaminant becomes more critical. Before PCB tissue congener analysis is determined to be necessary there should be a "reason to believe" that PCBs may pose an unacceptable bioaccumulation risk. In addition, any existing tissue data for the watershed should be considered in determining whether PCBs may present an unacceptable bioaccumulation risk. These issues are currently being evaluated in the Bioaccumulation Subcommittee (see Issue Paper: *Framework for Assessing Bioaccumulation Under RSET*).

REFERENCES:

Nedoff JA, Kennedy LJ, Williams BA. 2004. How Many PCB Congeners are Really Needed to Estimate Totals? Platform presentation at the Pacific Northwest SETAC Conference, Port Townsend, WA, April 14-16, 2004. Kennedy/Jenks Consultants, San Francisco, CA.

NOAA. 1989. Standard Analytical Procedures of the NOAA National Analytical Facility. 2nd ed. NOAA Tech. Memo. NMFS F/NWC-92, 1985-86. Contact: National Status and Trends Program, National Oceanic and Atmospheric Administration, NOAA N/OMA32, 11400 Rockville Pike, Rockville, MD 20852.

RECOMMENDATION:

Proposal:

1. Sediments would continue to be analyzed for total PCBs – this is the best determinant of direct toxicity to benthos.

2. Tissue would be analyzed for PCB congeners for assessment of risks to fish and bioaccumulative risks – options include laboratory bioaccumulation tests, *in situ* testing using caged bivalves/fish, and collection of resident species from the area.

3. Recent research would be used to correlate total PCB values in sediments to an equivalent total PCB value based on congener results in tissue, should it be necessary to do so to establish site-specific cleanup levels in sediment based on bioaccumulation pathways.

Next Steps:

1. Sediment Guideline Subcommittee and Bioaccumulation Subcommittee to develop appropriate screening levels for total PCBs in sediment and PCB congeners in tissue, as well as criteria for establishing "reason to believe" that PCBs may pose an unacceptable bioaccumulation risk.

2. With input from the Bioaccumulation Subcommittee on target tissue levels for PCB congeners, the Chemical Analyte Subcommittee will recommend an analytical method which provides an appropriate level of sensitivity (see White Paper on PCB Congener Analytical Methods).

3. Efforts should be made to document existing tissue and sediment data on PCB concentrations for watersheds in the Northwest. In particular congener analysis should be compiled in a database and made easily accessible to parties who may be involved in dredging or environmental investigations.

4. An outreach effort to the Department of Health should be initiated to determine how they plan to evaluate PCBs in tissue and the levels they will use to establish fish advisories.

PROPOSED LANGUAGE:

Section 8.4.1.

<<Add the following paragraph>>

Different analytical methods are required for analysis of PCBs in bulk sediment and tissue matrices. Bulk sediment will be analyzed for Aroclor composition using EPA Method 8082. If bioaccumulation testing is required, tissue samples will be analyzed for individual congeners (or a subset of congeners) using EPA Method [8082 or 1668, to be determined].

Table 8-2.

Revise Table 8-2 to add PCB congener method for tissue analysis and add footnote explaining different methods will be used for bulk sediment and tissue analysis.

Table 1. PCB Analytical Methods and Costs

Method	Detector	Detection limits	Cost	Analytes detected**	Comments
EPA 8082	ECD, Dual column for confirmation	~0.1-0.3 ug/kg	$225-350	~62 congeners with one injection (dual column), All 19 Coplanars	Possible interference include chlorinated pesticides, phthalates, polychlorinated terphenyls
EPA 680	Mass Spec	~0.2 ug/kg	$400-600		Some problems with identification due to co-elutions and presence of PCTs or other similar analytes

EPA 1668	Hi Res MS	~0.002-0.050 ug/kg	$750-1150	All 209 congeners, All 19 Coplanars	Most comprehensive based on detection selectivity
Krahn et al, 1994	HPLC/ Photodiode array	~1-4 ug/kg	$425-560	16 congeners, 12 Coplanars 77, 105, 118, 126, 128, 138, 156, 157, 169, 170, 180, and 189	Limited availability, Possible interference by PCTs, and PCNaphthalenes

*Typically dependent on the number of congeners requested.
**All methods include some co-elutions.
The 19 PCB co-planar congeners are:
Co-planars: Nos. 77, 81, 126, 169,
Mono-ortho coplanars: Nos. 60, 105, 114, 118, 123, 156, 157, 167, 189
Di-ortho co-planars: Nos. 128, 138, 158, 166, 170, 180

PCB Congener co-elution is not a static condition, and will vary between laboratories based on GC operating conditions, column conditions, etc., while still adhereing to the guidance put forth by the EPA methodology.

Table 2. PCB Congener Lists that Account for 80 Percent and 50 Percent of Total Congeners in Seven Sample Types* Collected from Portland Harbor

80% List	50% List	Congener on list from only one matrix	NOAA List (18)	12 Dioxin-like (coplanar)
1		crayfish		
4		crayfish		
18/30**			18	
20/28			20	
31				
40/41/71				
44/47/65	44/47/65	sculpin	44	
49/69				
52	52		52	
56				
61/70/74/76	61/70/74/76			
64				
66	66		66	
83/99	83/99			
84		sediment		
85/116/117				
86/87/97/108/119/125	86/87/97/108/119/125	sediment		
90/101/113	90/101/113		90	
92				
93/95/98/100/102	93/95/98/100/102	sediment		
105			105	105
110/115	110/115			

118	118		118	118
128/166		sediment	128	
129/138/160/163	129/138/160/163		129	
132				
135/151/154	135/151/154	carp		
136		carp		
141				
146				
147/149	147/149			
153/168	153/168		153	
156	156	crayfish		156
158		bullhead		
170	170		170	
171/173				
174	174	carp		
177				
178		bullhead		
179		carp		
180/193	180/193		180	
183/185				
187	187		187	
194				
196			.	
198/199				
83 congeners not including coplanars not in 80% list	45 congeners not including coplanars not in 50% list			
			8	
77	77		77	77
81	81			81
114	114			114
123	123			123
126	126		126	126
157	157			157
167	167			167
169	169		169	169
189	189			189
92 including coplanars not in top 80% list	54 including coplanars not in 50% list		18 total	12 total

* Seven sample types for which PCB Congener data were available in Round 1:
Sediment, Crayfish, Sculpin, Smallmouth Bass, Black Crappie, Brown Bullhead, and Carp (tissues were whole body)

** X/X/X Indicates group of coeluting congeners.

Highlighted cells indicate dioxin-like congeners.

Congener counts include coeluting congeners.

Methods:

1. Averaged the detected concentrations of each congener in each sample type

2. Totaled the average concentrations for each sample type (total PCB value)
3. Normalized the concentration against the total for each detected congener (% of total)
4. Ranked the congeners from highest to lowest normalized concentration (%)
5. Determined which congeners accounted for 80% and 50% of total for each sample type
6. Compiled list of all congeners in top 80% and top 50% for each sample type

Notes:
A. If apply 80% list to averaged, normalized list (in step 4), result is 86 - 89% of total for each sample type
Multiply total from 80% list by 1.2 to get total PCBs as congeners
B. If apply 50% list to averaged, normalized list (in step 4), result is 65 - 70% of total for each sample type
Multiply total from 50% list by 1.5 to get total PCBs as congeners

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